Studies on the Behavior of Mixed-Metal Oxides: Structural, Electronic and Chemical Properties of $MgMoO_4$, $FeMoO_4$ and $NiMoO_4$

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Introduction: Mixed-metal oxides play a relevant role in many areas of chemistry, physics and materials science. In principle, the combination of two metals in an oxide matrix can produce materials with novel chemical and physical properties that can lead to a superior performance in technological applications. In principle, several variables could be adjusted to control the performance of a mixed-metal oxide. To do this, one needs to obtain a fundamental understanding of phenomena that determine the behavior of bimetallic oxides. $MeMoO_4$ compounds (Me= Mg, Pb, Mn, Fe, Co, Ni, Zn) are ideal for studying the behavior of mixed-metal oxides and constitute and interesting group of compounds due to their structural, electronic and catalytic properties [1,2].

Methods and Materials: Time-resolved x-ray diffraction (TR-XRD), x-ray absorption near-edge spectroscopy (XANES) and first-principles density functional (DF) calculations were used to study the properties of $MgMoO_4$, $FeMoO_4$ and $NiMoO_4$.

Results: Nickel molybdate can exist in two phases (α and β) [1]. Mo is near a tetrahedral environment in the β-phase, whereas in the α-phase the metal exhibits a pseudo-octahedral coordination with two very long Mo-O distances (2.3-2.4 Å). The results of DF calculations indicate that the α-phase of $NiMoO_4$ is ~ 9 kcal/mol more stable than the β-phase. For the α → β transition in $NiMoO_4$, the DF calculations predict an energy barrier of ~ 50 kcal/mol. An apparent activation energy of ~ 80 kcal/mol can be derived from time-resolved XRD experiments. In the cases of $MgMoO_4$ and $FeMoO_4$, α-type phases are unstable and β-phases are observed over a large range of temperatures (20-700 C) [1,2]. The DF results and Mo L_{II}-edge XANES spectra show big differences in the splitting of the Mo 4d orbitals in the α and β phases of the molybdates. The line shape in the O K-edge essentially reflects the behavior seen for the 4d orbitals in the Mo L_{II}-edge (i.e. mainly O 1s → Mo 4d electronic transitions). The Mo L_{II}- and O K-edge in XANES can be very useful for probing the local symmetry of Mo atoms in mixed-metal oxides. The degree of ionicity in $MgMoO_4$ is larger than in $FeMoO_4$ or $NiMoO_4$. A correlation is found between changes in the electronic and chemical properties of β-$MgMoO_4$, β-$FeMoO_4$ and β-$NiMoO_4$ [1,2]. β-$NiMoO_4$ exhibits a large density of metal states near the top of its valence band and a substantial reactivity toward H_2 or H_2S. β-$MgMoO_4$ displays completely opposite trends, and β-$FeMoO_4$ is an intermediate case between the two extremes.

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